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**DEVELOPMENT OF SILICONE RUBBERS FOR USE  
AT TEMPERATURES DOWN TO -100° F.**

**U. S. GOVERNMENT CONTRACT DA-44-109-QM-64**

**PROGRESS REPORT**

**FOR THE PERIOD**

**MARCH 5, 1950 to JUNE 4, 1950**

**CONNECTICUT HARD RUBBER COMPANY**

**NEW HAVEN, CONNECTICUT**

THE CONNECTICUT HARD RUBBER COMPANY

NEW HAVEN, CONNECTICUT

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CONNECTICUT HARD RUBBER CO., NEW HAVEN

DEVELOPMENT OF SILICONE RUBBER FOR USE AT TEMPERATURES  
DOWN TO -100° F. - PROGRESS REPORT FOR THE PERIOD MARCH  
5-JUNE 4, 1950

B. J. HUMPHREY; ARNOLD PFENNINGER, JR.; CHARLES A. WALKER;  
AND OTHERS AUG '50 32PP. TABLES, GRAPHS

USA CONTR. NO. DA-44-109-QM-64

MATERIALS (8)

RUBBER, NATURAL AND SYNTHETIC (3)

RUBBER, SYNTHETIC

MATERIALS - LOW

TEMPERATURE

APPLICATION

RUBBER - TESTING

MATERIALS - IMPACT

TESTING

UNCLASSIFIED

AUGUST 25, 1950

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### SUMMARY

The immediate purpose of the work performed during the period covered by this report has been to improve or alter the nature of the commercially developed silicone rubbers so that the altered compounds will compare more favorably with hydrocarbon rubbers insofar as such physical properties as tensile strength, elongation and abrasion resistance are concerned.

Studies on the various types of pigments have been continued with the investigation of new pigments at the standard 25 volume loading, as well as the study of these and other pigments at variable loadings. Milling and handling techniques have been developed to give improved reproducibility of the physical test data on the resulting stocks.

The continuation of studies involving the synthesis of several silicone carboxylic and sulfonic acids as possible wetting agents has not yet produced sufficient information to permit a definitive appraisal of these materials.

Techniques have been developed during the past months for obtaining electron micrographs of both pigments and cured rubber specimens. Interpretation of these results is being deferred to a subsequent report inasmuch as the studies are only partially completed. The electron microscope is currently being used to study the cured rubber resulting from a new method of dispersing pigments in the gum, described below.

During studies on the solubility of silicone gum in titanium tetrachloride, it was found that the latter solvent,

even in small percentages, is capable of depolymerizing the silicone elastomer to a free-flowing liquid. More striking is the action of dry hydrogen chloride on the gum. By passing dry HCl gas over shredded silicone gum, the latter is converted easily to the liquid state. Repolymerization with regeneration of a gum, is brought about by bubbling nitrogen through the fluid, by applying heat, or by allowing it to stand in air.

These observations suggest such processing possibilities as follows: The regenerated gum may be compounded with a series of pigments in order that the difference between it and the original gum may be studied. The pigment may be incorporated into the gum while it is in the liquid state. Chemical action such as chlorination may be effected on this depolymerized gum. This approach has been discussed previously, but limitations due to the difficulty of reacting the gas with a solid have thus far prevented such a study. Possible chemical reactions on this chlorinated gum are the reaction with basic oxides to give crosslinking and the formation of organo-metallic derivatives also for crosslinking.

Solvent extraction of the silicone gum (GE 9979-G) has been accomplished with five solvents of several types in order to remove the fraction of the gum containing the lowest molecular weight material. The solvents did not appear to be selective as each removed the same quantity (18-20%) with a second stage removing only a small fraction more. The physical test results on the stocks compounded from the gums after being extracted were not improved; in fact, they were somewhat inferior to similar control compounds.



In order to evaluate the use of selenium dioxide as a curing agent, an investigation has been made of the action of  $\text{SeO}_2$  on simple siloxanes, silicone oils and on the silicone gum. Fundamental studies on the oxidation of hexamethyl-disiloxane with  $\text{SeO}_2$  have produced several oily products which are being characterized, a process which will be assisted by infra-red analysis. Action of  $\text{SeO}_2$  on low viscosity silicone oils has yielded products more viscous than the starting material and which are capable of forming gums when treated with ferric chloride. The gum-forming capabilities of these  $\text{SeO}_2$  treated oils are superior to those of the original silicone oils which were studied as a control.

Silicone gum (GE 9979-G) has been milled with 56 parts of Celite 505 and 10 parts of  $\text{SeO}_2$  and press cured under a temperature condition in which a control sample containing no curing agent yields a crumbly, unknitted mass. These preliminary results show a definite curing action by this oxidizing agent and indicate that further studies will be fruitful.

Preliminary experiments on the hydrolysis of dimethyl-dichlorosilane in water or solutions of polyfunctional alcohols and subsequent treatment of the oils have resulted in gums which are being evaluated at the present time.

## INTRODUCTION

Investigations have been carried out by the Connecticut Hard Rubber Company on the adaptation of commercially developed silicone gums for use at low temperatures. These silicone gums when compounded with a suitable pigment and a curing agent have physical properties as measured by tensile strength, elongation, and abrasion resistance inferior to those of conventional hydrocarbon rubbers. The immediate aim of the research program has been to improve the physical properties of the compounded rubber by either physical or chemical treatment of the gum or pigments. An outline of the research program for the period covered by this progress report follows:

- I. Studies of pigments involving the selection of the proper pigment and loading as well as alteration of the pigment-silicone gum interface.
- II. Synthesis of a silicone base wetting agent for the pigment-silicone gum system.
- III. Studies of pigments and their dispersion in silicone rubber by the electron microscope.
- IV. Depolymerization of silicone gum leading to the possibilities of chemical action and better pigment incorporation.
- V. Removal of volatile oils from the gum by solvent extraction.
- VI. Reaction of the silicone gum to various curing agents with special emphasis on the use of selenium dioxide.
- VII. Studies on the preparation of silicone gums from commercially available oils and from the various monomers.

## I. STUDIES OF PIGMENTS

The evaluation of various pigments as reinforcing agents for silicone rubber continues to be an integral part of this project. As new pigments become available they are compounded in various volume loading either as-received or after pretreatment. This phase of the program also serves to develop and improve the technique for handling silicone rubber.

### A. Pigments as-received, 25-volume loading

Six new pigments (Alon II and a series of iron oxides) have been evaluated during this period. The test results are shown in Table 1 and Figure 1; properties of the pigments, insofar as they are available, are listed in Table 2. Alon II appears to be somewhat inferior to the Alon previously tested. Mapico Crimson 88 and Mapico Brown 418 seem to be somewhat superior to iron oxides previously tested in that they yield softer stocks with higher tensile strengths.

### B. Pigments after pretreatment, 25-volume loading

Alon was wetted with a benzene solution of benzoyl peroxide containing peroxide equivalent to 2 parts per 100 parts of gum in a stock with a 25-volume loading of Alon. The benzene was removed by evaporation at room temperature. The peroxide-coated Alon was then used in compounding stocks with and without additional benzoyl peroxide. The effect of this treatment, intended to cause some of the curing to occur at the pigment-rubber interface, was unfavorable because of an alteration in

physical structure of the pigment which occurred as a result of wetting with benzene. The physical test data are presented in Table 3.

C. Pigments as-received or pretreated, variable volume loading

Nine pigments which were indicated in the 25-volume loading studies to be of some promise were compounded at other volume loadings with the results shown in Table 4 and Figures 2, 3 and 4. The physical properties of these pigments have been listed in previous reports. In general, the stocks showed increasing hardness, increasing tensile strength and decreasing elongation as the loading was increased. An interesting exception is Whitcarb R which showed an increase in elongation under the same conditions. The results of continuing experiments with this pigment will be detailed in future reports.

D. Mixture of Pigments

Mixtures of Protoc 166 and Rayox 110 have been investigated with the results shown in Table 5 and Figure 5. The properties of the stocks remained essentially unchanged as the relative quantities of the two pigments were varied.

E. Milling Techniques

In the previous progress report there was included a discussion of the reproducibility of physical properties of a stock containing 100 parts by weight of gum (G.E. 9979-G), 50 parts by weight of Celite 505 and 2 parts of benzoyl peroxide. Statistical analysis of the results obtained on 106 batches of this stock gave the following results:

	Minimum Value	Maximum Value	Mean Value	Probable Error
Hardness	31	59	43	4
Tensile	50	360	203	36
Elongation	62	275	132	24

It will be recalled that the probability is 0.50 that the true value of a property lies within the range of the mean value plus or minus the probable error.

During the period May 1 to June 2, an additional 40 batches of the standard stock were prepared and tested with the following results:

	Minimum Value	Maximum Value	Mean Value	Probable Error
Hardness	30	57	45.7	3.7
Tensile	172	294	226.4	19.7
Elongation	75	167	118.9	15.6

It will be noted that these last tests show a probable error in the hardness value roughly equal to that first obtained, but that the probable error in tensile strength is only about one-half of the value previously obtained, and the probable error in elongation is approximately two-thirds of the value derived in the first study. This improvement is the result of a combination of factors which can be summarized as improved techniques. However, further pursuit of this investigation is not planned because it is felt that the lack of reproducibility is due simply to the fact that we are dealing with a stock having low values of tensile strength and elongation, and that small absolute differences in physical properties lead to relatively large percentage errors. As stocks are improved this difficulty might be automatically eliminated.

TABLE I  
Studies of As-Received Pigments at 25-volume loading

<u>Pigment</u>	<u>Compound No.</u>	<u>Parts Pigment Per 100 Parts Gum</u>	<u>Hardness Shore A</u>	<u>Tensile Strength psi</u>	<u>Elongation Percent</u>
Alon II	1375	98	34 34	116 160	175 187
Mapico Black	1410	148	44 42	169 105	137 100
Mapico 100 Yellow	1406	148	42 38	232 152	162 175
Mapico Yellow Dark Orange	1407	148	40 41	143 178	112 137
Mapico 88 Crimson	1408	148	42 45	254 278	137 150
Mapico 418 Brown	1409	148	45 42	217 223	137 187

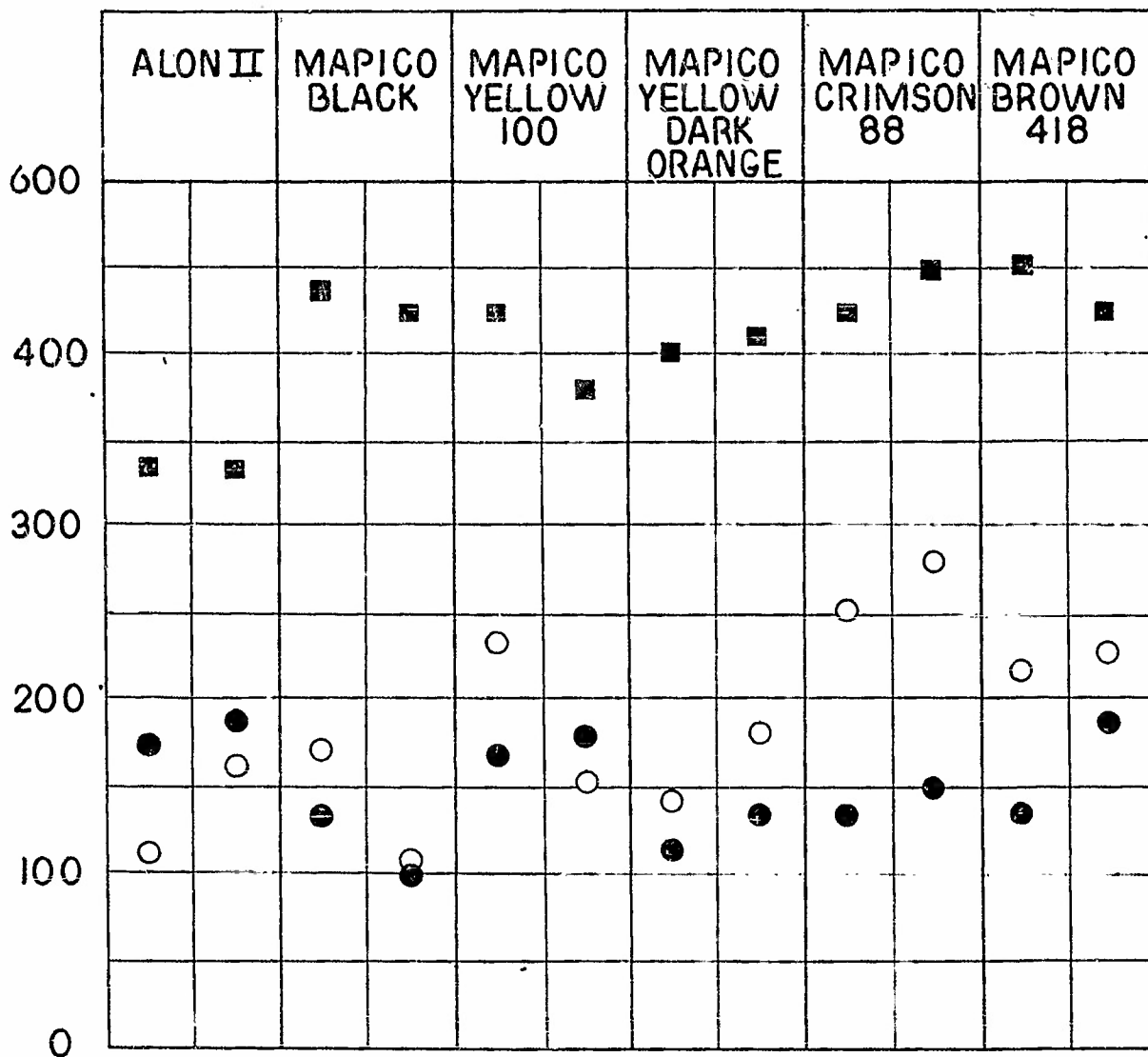


FIGURE-1 PIGMENTS AS RECEIVED

CONNECTICUT HARD RUBBER COMPANY

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DA-44-109-QM-64

○ = TENSILE-P.S.I.  
● = ELONGATION - %  
■ = HARDNESS-x 10  
SHORE A

TABLE 2

Properties of Pigments  
Tested

<u>Pigment</u>	<u>Composition</u>	<u>Supplier</u>	<u>Specific Gravity</u>	<u>Average Particle Size, Microns</u>	<u>pH</u>
Alon II	Aluminum Oxide	G.L. Cabot	3.60	0.005 - 1.0	-
Mapico Black	Iron Oxide	Binney & Smith	4.95	0.2	7.5
Mapico Yellow 100	" "	"	4.05	0.1 - 0.8	6
Mapico Yellow Dark Orange	" "	"	4.09	0.1 - 0.8	6
Mapico Crimson 88	" "	"	4.58	0.2 - 0.6	6
Mapico Brown 418	" "	"	5.2	-	-



TABLE 3

Alon Coated with Benzoyl Peroxide

<u>Additional Peroxide Added on Mill, Parts Per 100 Parts of Gum</u>	<u>Compound No.</u>	<u>Hardness Shore A</u>	<u>Tensile Strength psi.</u>	<u>Elongation Percent</u>
0	1417	32	100	225
		35	109	175
1	1413	44	173	175
		50	263	200
2	1414	52	371	200
		46	188	150
3	1415	59	251	100
		58	197	87
5	1416	65	243	75
		64	227	62

TABLE 4.

## Studies of Pigments at Variable Loading

Pigment	Compound No.	Volumes per 100 volumes Gum	Parts per 100 Parts Gum	Hardness Shore A	Tensile Strength psi	Elongation Percent
Fumo Silica	1357	10	22	25	55	156
	1358	20	43	36	116	112
	1120	25	53	37	91	137
	1359	30	64	51	163	81
	1360	40	86	55	181	69
Alon II	1375	25	98	34	138	181
	1392	38	147	41	269	194
	1393	50	196	50	261	181
	1484	75	294	60	381	134
	1485	100	392	81	355	38
Celite Snowfloss	1394	10	22	24	64	144
	1395	20	44	34	109	131
	1373	25	55	43	166	125
	1396	30	66	52	263	112
	1397	40	88	70	332	110
Celite Superfloss	1398	10	25	26	92	181
	1399	20	50	36	195	194
	1374	25	63	40	182	125
	1400	30	75	41	212	119
	1401	40	100	55	343	106
Whitcarb R	1353	10	29	25	38	119
	1354	20	58	35	59	81
	1107	25	72	30	63	200
	1355	30	87	41	158	162
	1356	40	115	41	194	237
Statex A	1402	10	19	18	76	269
	1403	20	39	28	122	187
	1328	25	49	40	155	131
	1404	30	59	39	225	181
	1405	40	79	54	325	150
Mapico Crimson 88	1418	10	59	37	169	162
	1408	25	148	44	266	144
	1419	40	237	72	279	87
Mapico Black	1421	10	59	36	51	87
	1410	25	148	43	137	119
	1420	40	237	77	412	69
Mapico Brown 118	1422	10	59	33	59	137
	1409	25	148	44	220	162
	1423	40	237	52	170	119

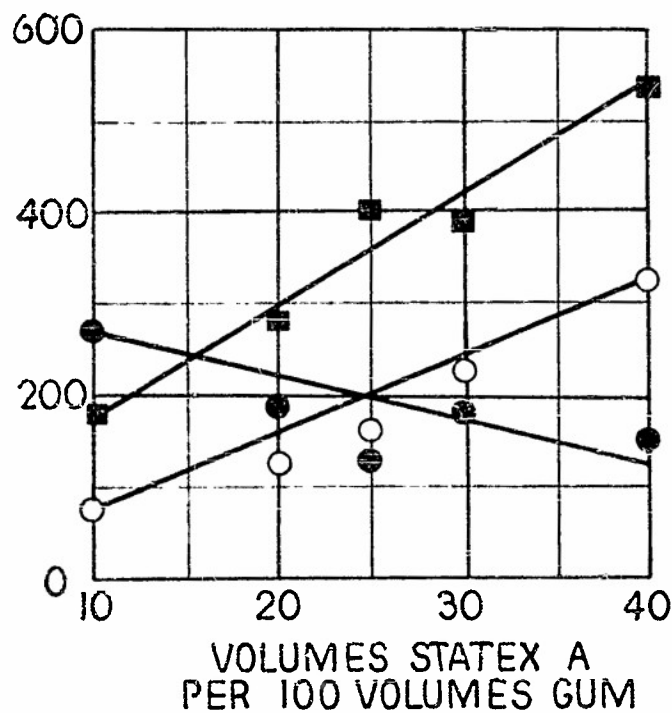
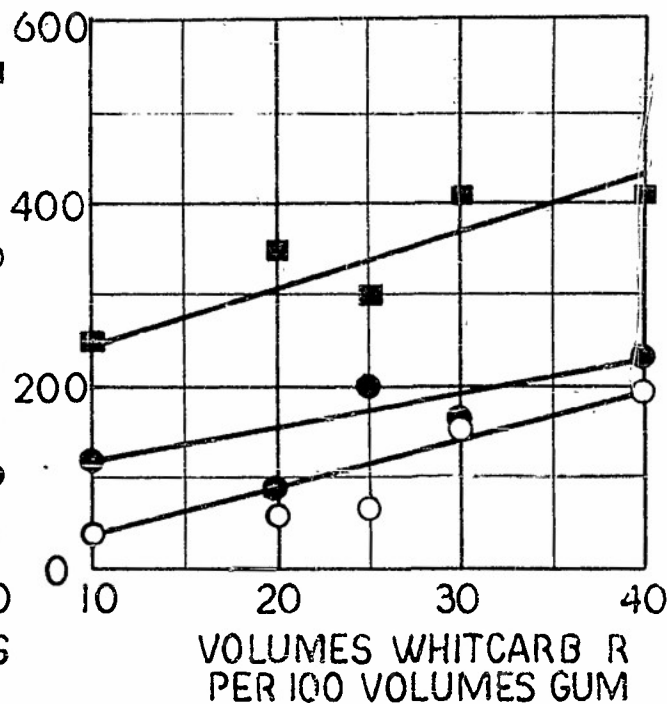
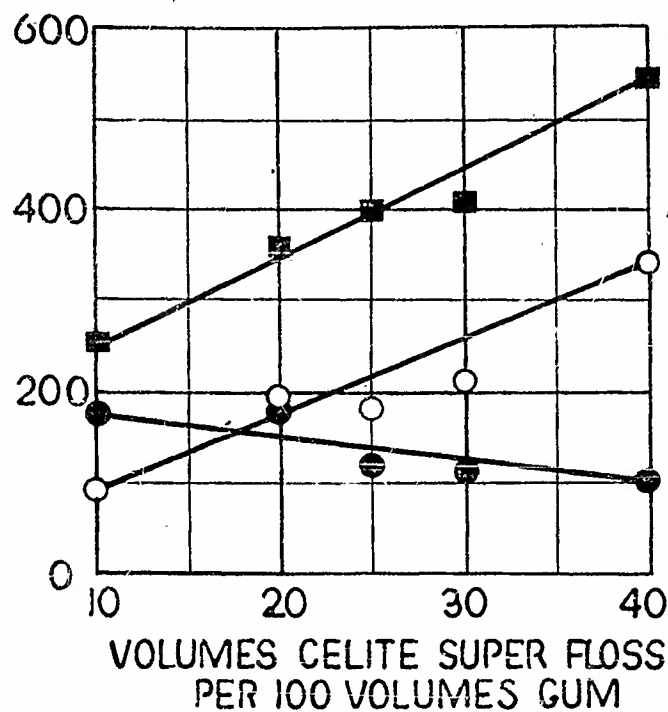


FIGURE -2  
VARIABLE VOLUME LOADING

CONNECTICUT HARD RUBBER  
COMPANY

U.S. GOVERNMENT CONTRACT  
DA-44-109-QM-64

○ = TENSILE - P.S.I.  
● = ELONGATION - %  
■ = HARDNESS x 10  
SHORE A

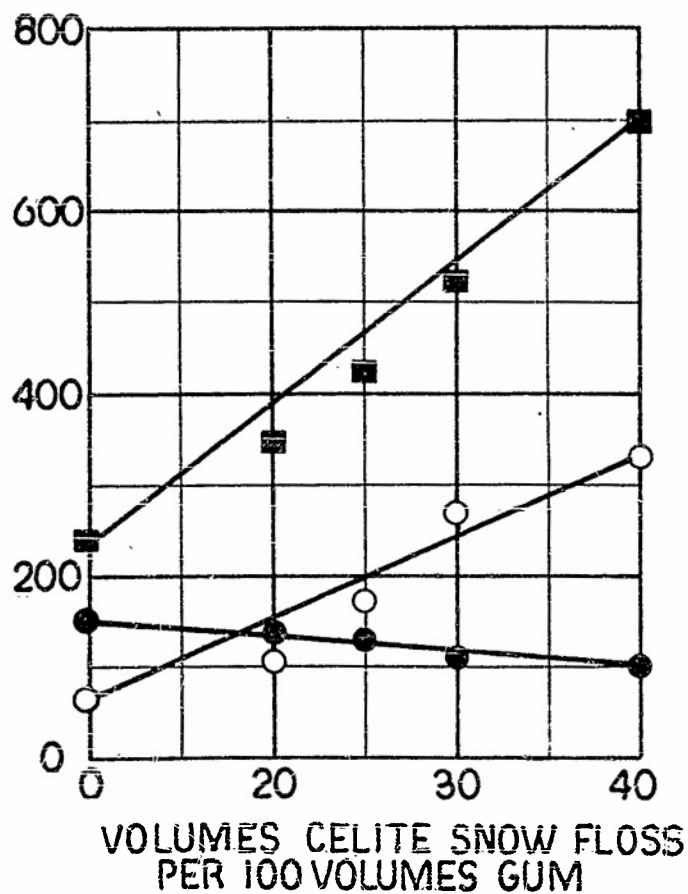
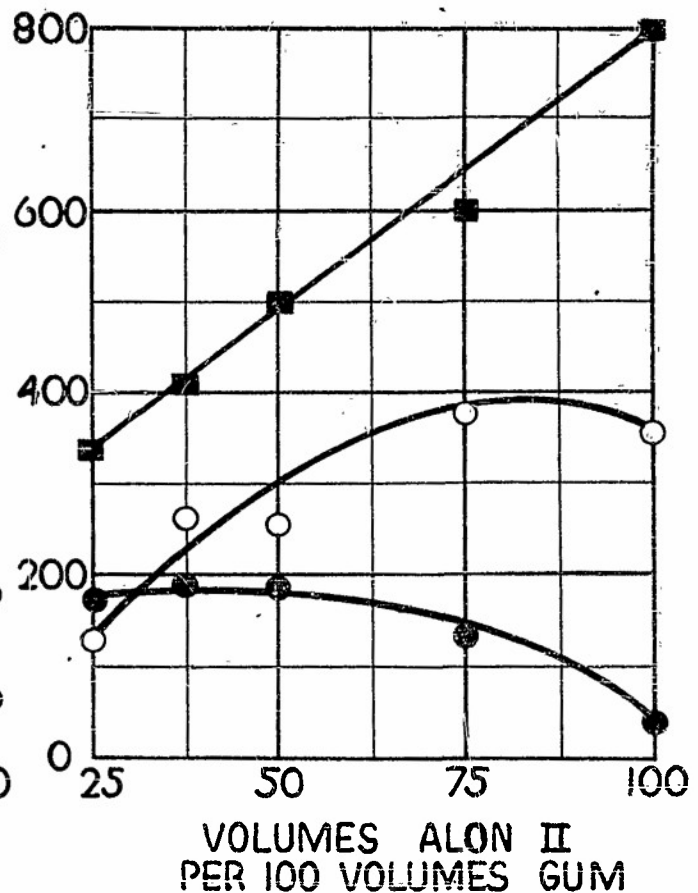
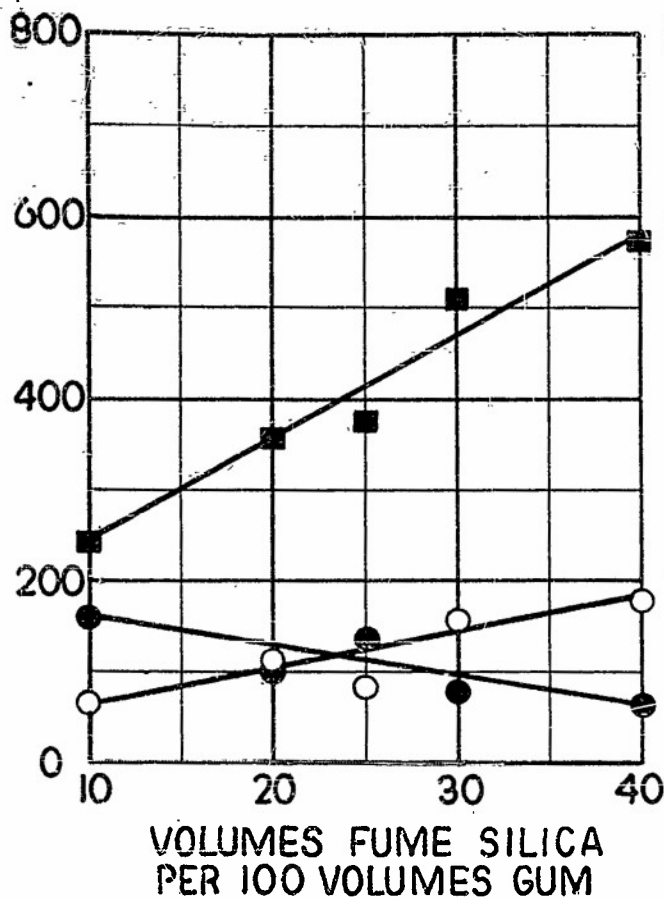


FIGURE-3  
VARIABLE VOLUME LOADING

CONNECTICUT HARD RUBBER  
COMPANY

U.S. GOVERNMENT CONTRACT  
DA-44-109-QM-64

○ = TENSILE - P.S.I.  
● = ELONGATION - %  
■ = HARDNESS × 10  
SHORE A

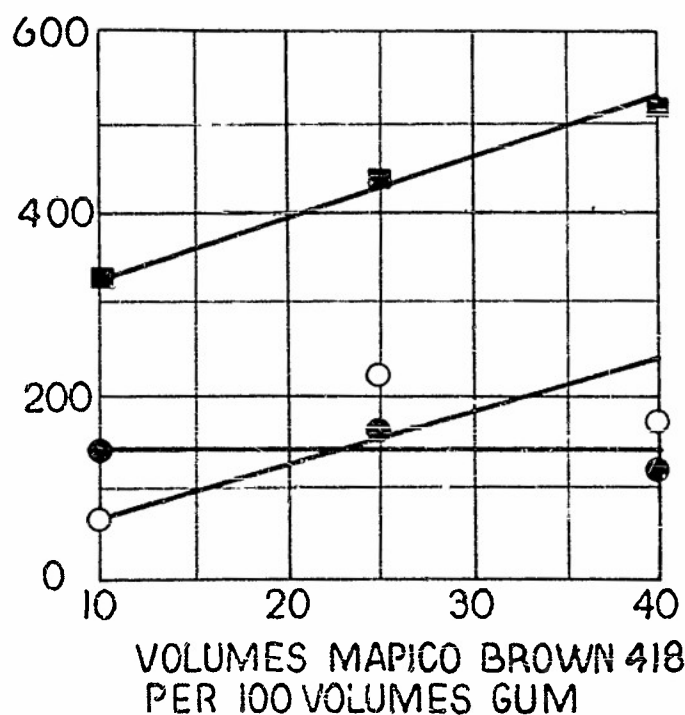
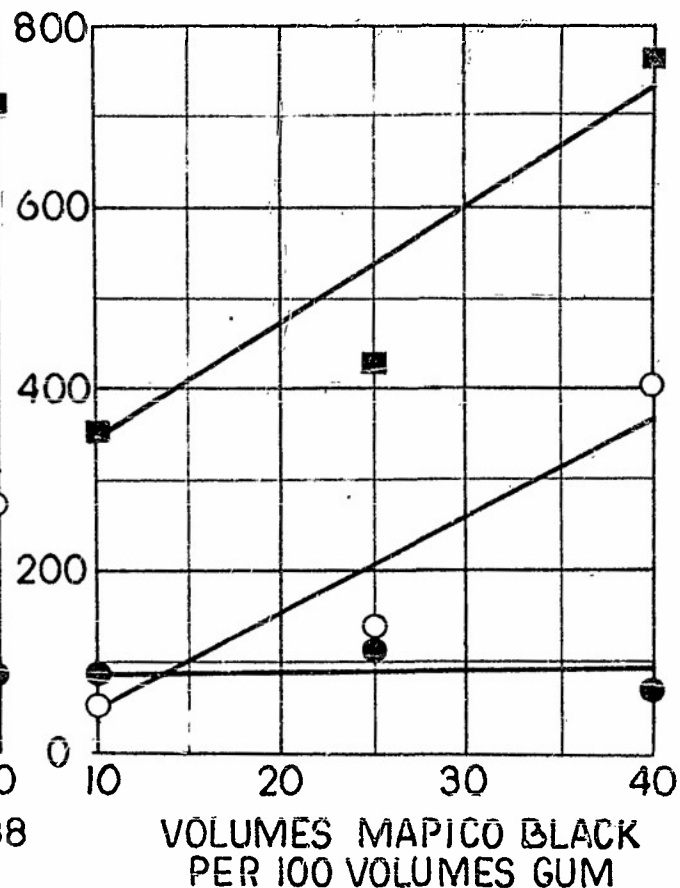
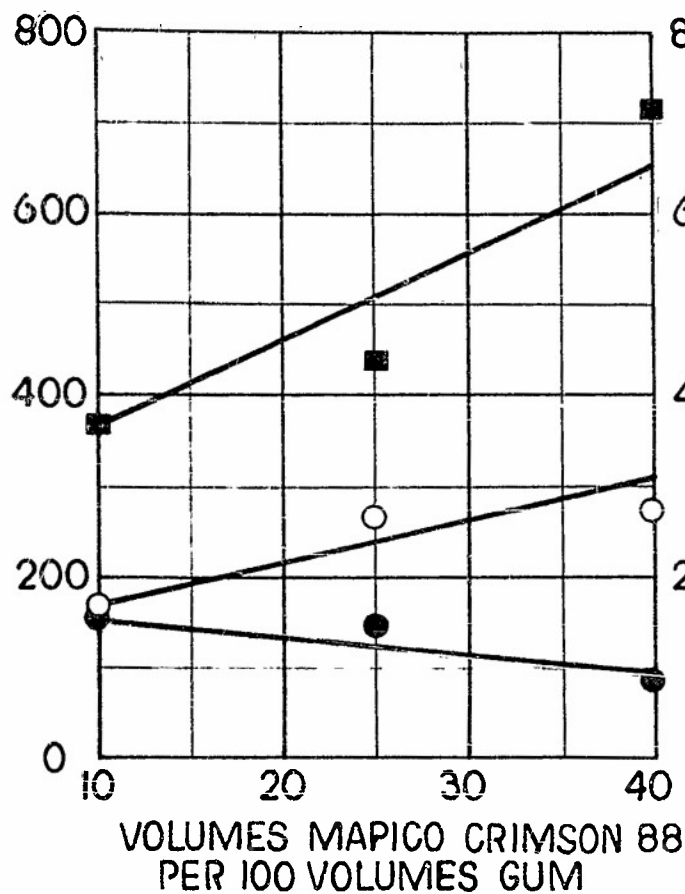


FIGURE - 4  
VARIABLE VOLUME LOADING

CONNECTICUT HARD RUBBER  
CONNECTICUT  
U.S. GOVERNMENT CONTRACT  
DA-44-109-QM-64

○ = TENSILE - P.S.I.  
● = ELONGATION - %  
■ = HARDNESS × 10  
SHORE A

TABLE 5  
Mixtures of Pigments

Parts by Weight		Compound No.	Hardness Shore A	Tensile Strength psi.	Elongation Percent
<u>Protox 166</u>	<u>Rayox 110</u>				
0	100	1361	38	125	156
25	75	1381	33	109	188
37.5	62.5	1380	35	92	163
50	50	1379	34	102	194
62.5	37.5	1378	33	109	238
75	25	1377	33	103	219
100	0	1062	38	91	181

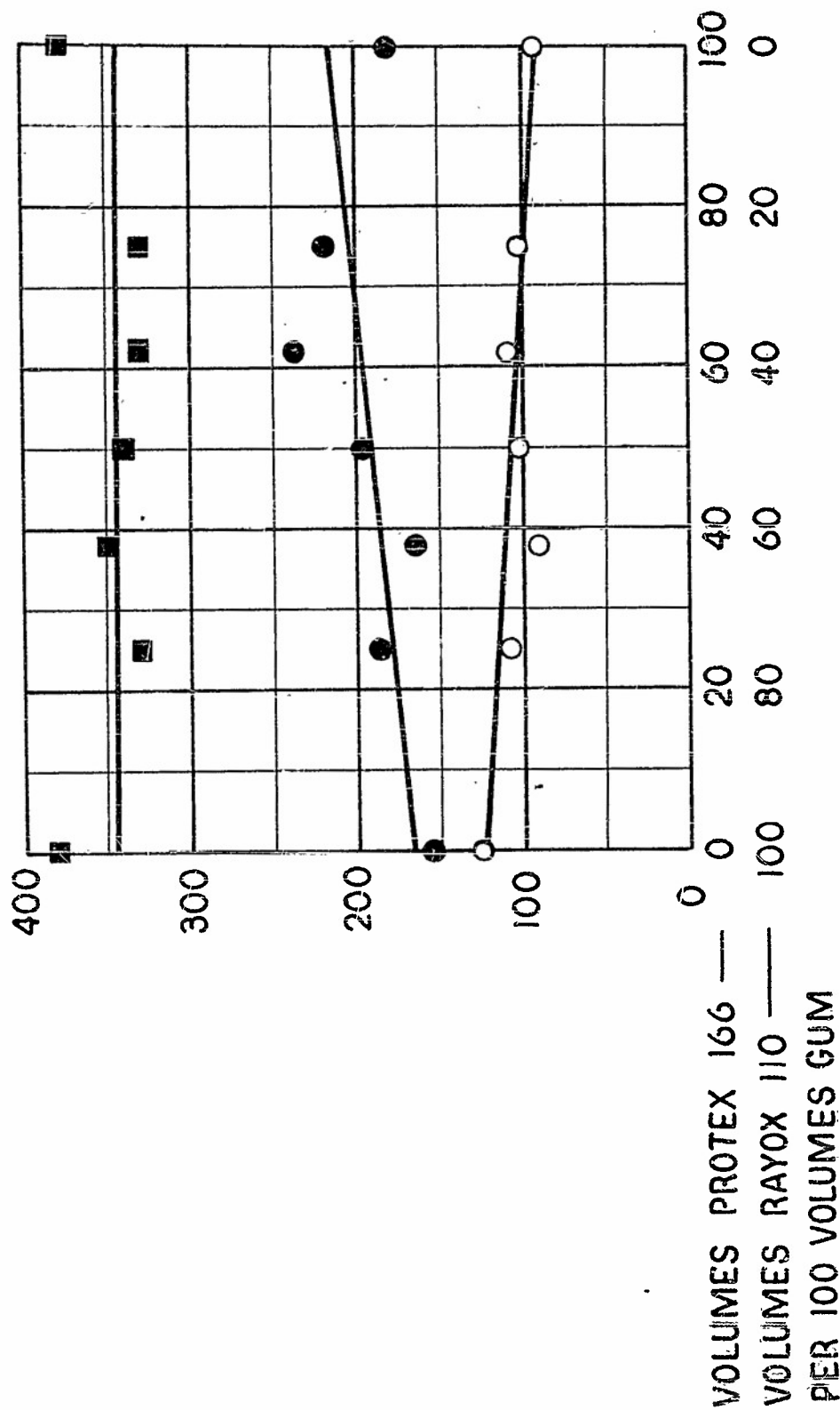


FIGURE-5 MIXTURES OF PIGMENTS

O = TENSILE - PS.I.  
 ● = ELONGATION - %  
 ■ = HARDNESS x 10  
 SHORE A

CONNECTICUT HARD RUBBER COMPANY  
 U.S. GOVERNMENT CONTRACT DA-44-109-QM-64

## II. Wetting Agents for Pigment-Rubber Systems

Experiments in the preparation of long chain silicone-carboxylic acids have been continued. The use of such compounds as possible wetting agents for improving the pigment-rubber bond has been discussed in earlier reports. Mention will be made here of several approaches to the preparation of silicone units with carboxylic acid or sulfonic acid functions.

The preparation and testing of a simple silicon-carboxylic acid, p-trimethylsilylbenzoic acid, has been reported previously. More recent investigations on the preparation of long chain silicone counterparts of stearic acid are described below.

The hydrolysis of dimethyldichlorosilane in mixtures of water and allyl alcohol whereby  $-\text{OSi}-\text{O}-$  units would be introduced at intervals along the chain has been studied. The final oxidative-cleavage of the ethylenic links to furnish carboxylic acids has not as yet been performed successfully.

Hydrolysis of  $(\text{CH}_3)_2\text{SiCl}_2$  in aqueous glycolic acid has produced oils in which the  $\text{HO}-\text{CH}_2-\text{COOH}$  units have been incorporated. Test results on this product are not yet definitive and hence do not appear in this portion of the report.

Sulfonation experiments have been carried out on resin-like products from the hydrolysis of trichlorophenylsilane, and gummy polymers produced by the hydrolysis of dichlorodiphenylsilane. Under normal sulfonation conditions using  $\text{H}_2\text{SO}_4$ , no sulfonic acids have been isolated. Higher temperatures are to be employed and other sulfonating agents, such as chlorosulfonic acid, will be used in the continuation of this phase of the research program.



### III. ELECTRON MICROSCOPE STUDIES

The electron microscope is being used in the current program to obtain detailed information on the nature of the pigments employed and on the nature of the distribution of the pigments in silicone gum. Although electron micrographs of the pigments and of cured rubber specimens are being made successfully at present, and a number of both types have been prepared during this period, a clear interpretation of the results will not be possible until further work is done. Hence, the electron micrographs prepared during this period will be submitted at a later date when a better evaluation of the results is available.

#### IV. DEPOLYMERIZATION OF SILICONE GUMS

A particularly interesting development of this period resulted from studies on methods of dissolving silicone gum in titanium tetrachloride. It was hoped that the  $\text{TiCl}_4$ -gum solution could then be hydrolyzed to regenerate the gum and, at the same time, form  $\text{TiO}_2$  which would be very intimately mixed with the regenerated elastomer.

Initial experiments showed a surprisingly high solubility of gum in  $\text{TiCl}_4$ , with as little as 5%  $\text{TiCl}_4$  effecting the conversion of gum to a free-flowing liquid. It appeared that the  $\text{TiCl}_4$  was causing depolymerization, possibly by acid-type cleavage of the Si-O-Si linkages. Additional reason for considering this effect to be an acid-cleavage depolymerization was found in the action of dry hydrogen chloride on the gum. On passing dry HCl over a sample of shredded gum (G. E. 9979-G) the material gradually softened, became viscous and was converted in a few hours to the same type of free-flowing liquid observable in the  $\text{TiCl}_4$  experiments.

The above observations appeared more significant when it was found that the gum of the HCl depolymerized elastomer could be easily regenerated in a form substantially identical to the original material by employing any of the following three procedures;

1. Allowing the liquid to stand 24 hours at room temperature ( $70^\circ\text{F}$ )
2. Heating the fluid in an open beaker at  $100^\circ\text{C}$ . for one hour
3. Bubbling nitrogen through the depolymerized gum to sweep out the HCl

As a consequence of this method for converting gum to a state in which it can be readily repolymerized, more receptive to the blending of pigments, and more subject to the action of chemical agents, several courses of investigation are now opened. Four of the more promising are detailed below.

A. Alteration of Molecular Weight Distribution in the Gum

If the effect of dry hydrogen chloride gas on silicone gum is actually a depolymerization, then regeneration of the gum would be expected to lead to a change in the molecular weight distribution in the gum, but not necessarily in the average molecular weight. By varying the conditions of depolymerization and repolymerization, a degree of control over the molecular weight distribution may be obtained. It should be noted that the degree of control obtained here is possibly greater than that obtained in the original formation of the gum by condensation. Furthermore, the technique involved is easy to apply. This indicates that a systematic study of the effect of depolymerization and repolymerization conditions on the properties of the gum is desirable.

B. Chemical Reaction on the Gum

Methods for altering the chemical nature of the gum have been sought since the beginning of this program. One of the major difficulties has been the fact that chemical treatment of a solid material usually results in reaction

carry out a further reaction intended to introduce cross-linking groups. A tri-functional compound which would utilize two reactive groups in repolymerization of the gum, leaving the third group for cross-linking, should be sought.

## V. REMOVAL OF VOLATILE OILS FROM GUM

It has been suggested that the commercial method of preparing silicone gum is such that the gum might be expected to contain some relatively low-boiling silicone polymers. Such polymers might be expected to function as plasticizers and to improve the physical properties to some extent. If they were present in excess, however, the effect on certain physical properties might be unfavorable. It appeared advisable, therefore, to attempt removal of the low molecular weight portion of the gum to determine the possible effect of this fraction on physical properties. Of the three methods suggested for removal of this material (solvent extraction, molecular distillation and steam distillation), solvent extraction was judged the simplest for preliminary studies.

Three techniques were used for solvent extraction of the gum:

### 1. Solvent extraction without stirring.

A weighed batch of milled gum was placed in a 2-liter round bottom flask and 1000 ml. of solvent added. The mixture was refluxed for five hours after which time the excess solvent was removed by filtration. The swelled gum was placed in an evaporating dish and heated at 212°C. until no further change in weight occurred.

### 2. Solvent extraction with stirring.

This method is the same as the first except that a 3-neck flask was used to permit stirring of the mixture during refluxing.

### 3. Two-stage extraction

In some instances the gum recovered in the second process was extracted a second time using the same technique.

The results of these studies are presented in Table 6 and Figure 6.

In each instance, the recovered gum was compounded with 25 volumes Celite 505, using 2% benzoyl peroxide on the gum. It will be noted first that the recovery of gum in all cases was substantially the same and that the recovery was not decreased appreciably by a second extraction with carbon tetrachloride or benzene. These facts indicate that all of the solvents are selective for a portion of the gum, probably the low molecular weight portion.

It is evident that the effect of solvent extraction on the physical properties of the stocks is slight. It appears that the hardness might increase somewhat and that the tensile value decreases slightly. It is thus indicated that the low-boiling fraction of the gum has no markedly adverse effect on the physical properties of the gum.

TABLE 6  
Solvent Extraction of Silicone Gum 9979-G

<u>Solvent</u>	<u>Method</u>	<u>Percent Recovery</u>	<u>Compound No.</u>	<u>Hardness</u>	<u>Tensile</u>	<u>Elongation</u>
C Cl <sub>4</sub>	a	83.0	1436	45	163	94
C Cl <sub>4</sub>	b	82.5	1437	48 44	201 191	100 112
C Cl <sub>4</sub>	c	79.4	1455	44 45	168 168	100 108
C <sub>6</sub> H <sub>6</sub>	a	81.5	1438	43 40	172 165	106 106
C <sub>6</sub> H <sub>6</sub>	b	82.7	1439	40 42	185 221	117 158
C <sub>6</sub> H <sub>6</sub>	c	79.6	1456	45	172	142
C <sub>2</sub> Cl <sub>4</sub>	a	80.5	1440	46 47	180 181	92 100
C <sub>2</sub> Cl <sub>4</sub>	b	83.3	1441	58 53	170 231	83 100
CHCl <sub>3</sub>	b	82.8	1453	55 55	176 192	75 100
C <sub>7</sub> H <sub>8</sub>	b	83.2	1454	56 52	151 155	92 108
Untreated Gum (Average Values)			1072	46	226	119

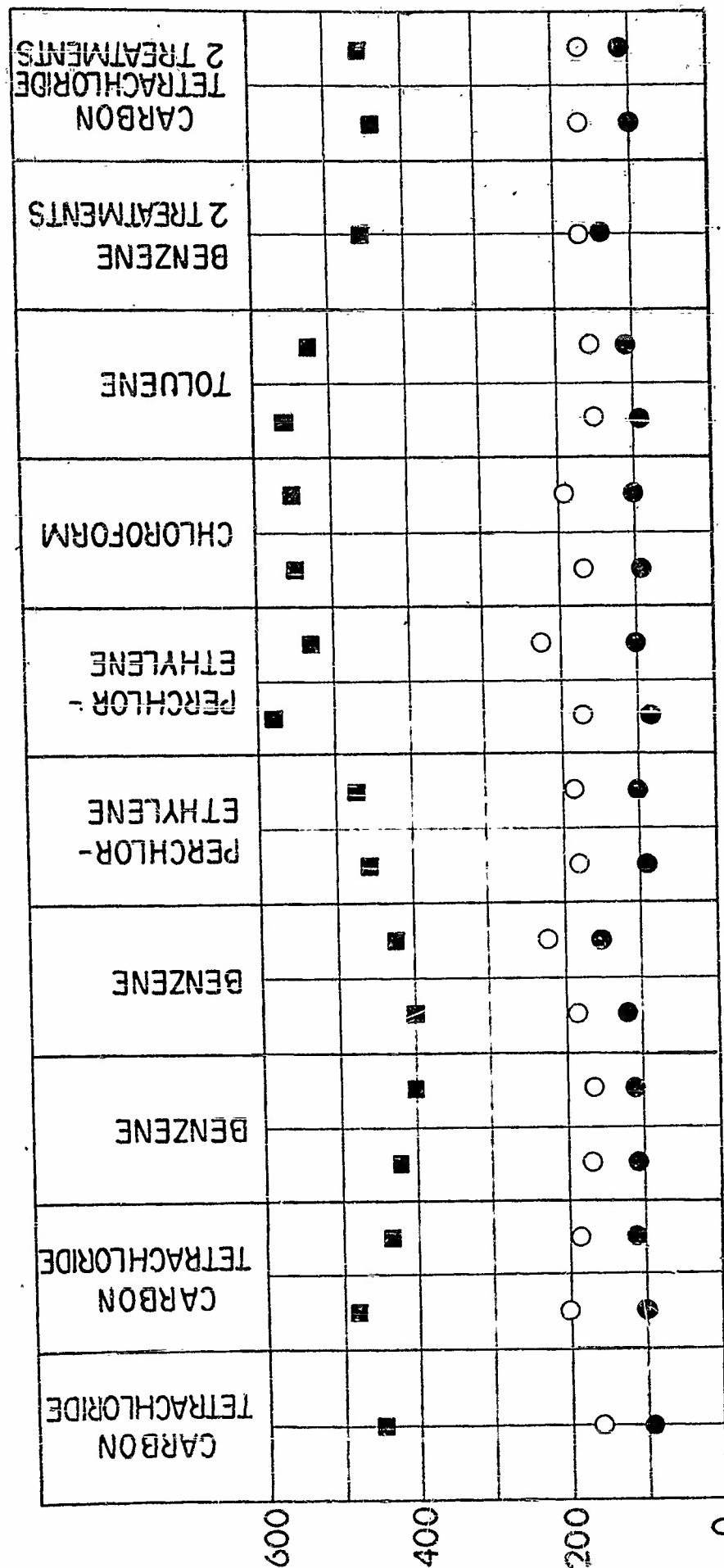


FIGURE -6 SOLVENT TREATMENT

O = TENSILE - P.S.I.  
 ● = ELONGATION - %  
 ■ = HARDNESS x 10  
 SHORE A

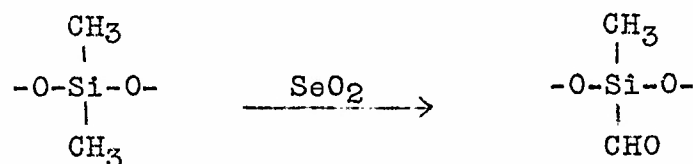
CONNECTICUT HARD RUBBER COMPANY  
 U.S. GOVERNMENT CONTRACT DA-44-109-QM-64

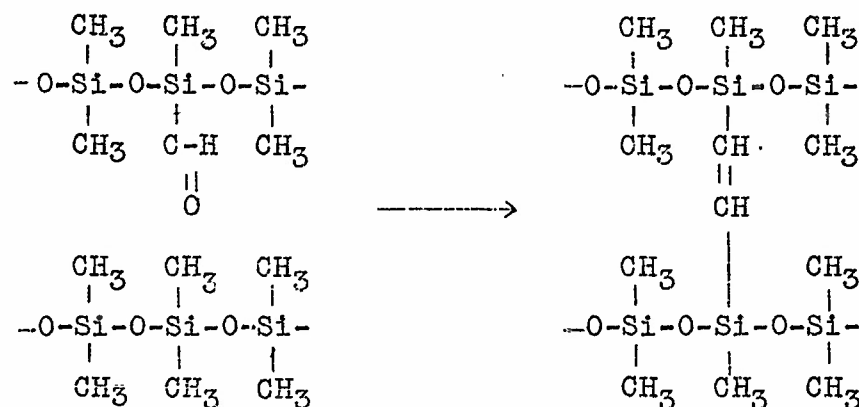


# VI. REACTION OF SILICONE GUM TO VARIOUS CURING AGENTS

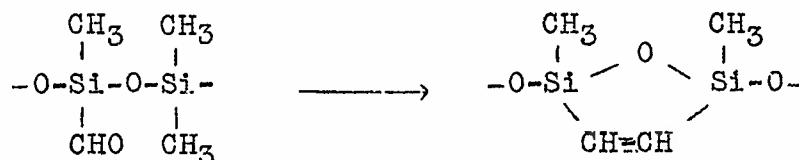
Methods superior to those in commercial use for initiating cross-linkage in silicone rubbers are being sought. During this period a few compounds (diisopropylbenzene hydroperoxide, cumene hydroperoxide, triethylenetetramine and hexamethylenetetramine) have been evaluated as possible substitutes for benzoyl peroxide. None of these compounds effected a cure when subjected to the same conditions under which benzoyl peroxide produces a satisfactory cure.

It was noted in the preceding progress report that selenium dioxide might be expected to function as a cross-linking agent for silicones. This material is commonly used as an oxidizing agent to convert active methylene groups to carbonyl functions. Theoretical grounds indicate that the methyl groups in the alpha position to Si in a silicone would, on treatment with selenium dioxide, yield a reactive site capable of intermolecular or intramolecular condensation. Intermolecular condensation would be of the aldol type and would be in the nature of a cross-linking:





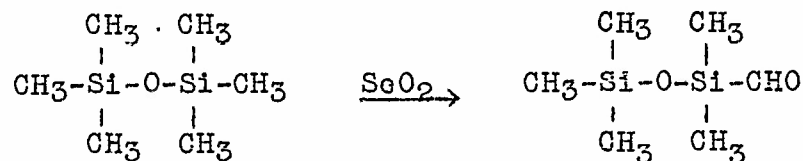
Intramolecular condensation might increase the intermolecular attraction between silicone chains by reducing the interference effect due to the highly mobile -Si-O bonds:

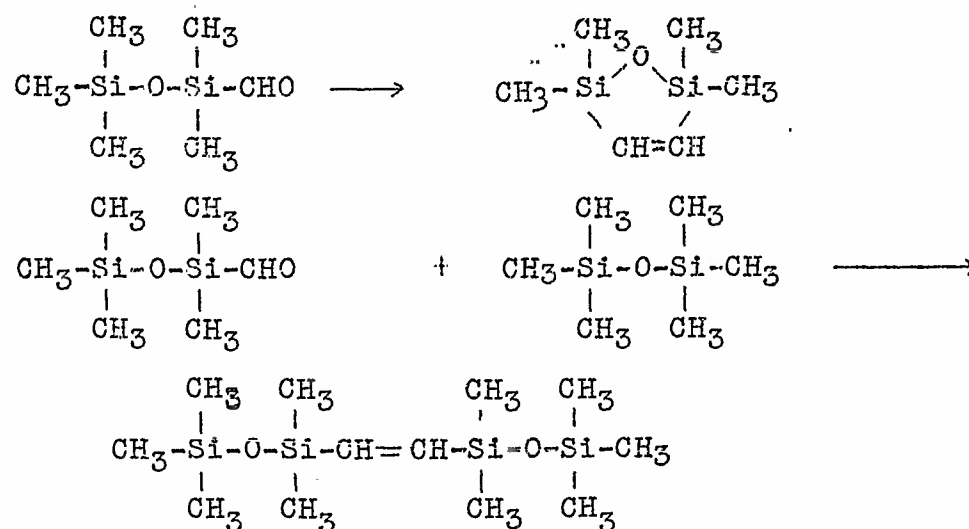


Results of the reaction of selenium dioxide on hexamethyl disiloxane, on low viscosity silicone oils and on gum samples as outlined below indicate a definite curing reaction:

A. Reaction of Hexamethyldisiloxane with Selenium Dioxide

To initiate studies on the effect of selenium dioxide on silicones, it was decided to determine first whether this material had any effect on a simple silicone of known structure. Some of the reactions which might occur with hexamethyldisiloxane are:





It was found first that selenium dioxide does not react at an appreciable rate with hexamethyldisiloxane at the boiling point of the latter (about 100°C.). A reaction did occur, however, when the reactants were heated in a sealed tube to 250°C. for 5 hours. A vigorous liberation of hydrogen selenide occurred with formation of metallic selenium. Two liquid phases and a solid phase were obtained. The oily phase has been fractionated and the fractions are being characterized in an attempt to determine the reaction scheme. A knowledge of this reaction scheme would be very valuable in planning studies on the effect of selenium dioxide in oils and gums.

#### B. Reaction of Silicone Oils with Selenium Dioxide

The second phase of the study of reactions occurring between silicone compounds and selenium dioxide has involved the use of silicone oils. The purpose of the studies on oils of low viscosity was to ascertain the effect of selenium dioxide on a system analogous to the

silicone chains in the gum. At the time of this work no method other than milling was available for dispersing  $\text{SeO}_2$  in gum. Therefore, it was planned first to investigate the curing action of  $\text{SeO}_2$  under conditions of maximum dispersion, such as would be obtained by vigorous stirring of the oxide in a liquid medium.

The results of the  $\text{SeO}_2$  oil reactions indicate that such treatment produces a pronounced increase in viscosity. In general, the gum forming capacity of the oils was not greatly enhanced by pretreatment with selenium dioxide, with the exception of G. E. oil 9981LT-35. Work is continuing both with oils of higher viscosity and the  $\text{SeO}_2$  treatment of hydrolysis products of dimethyldichlorosilane. Several oils have been studied, each being reacted with selenium dioxide for several hours in a reflux system at atmospheric pressure. The product in each instance was treated with ferric chloride in an attempt to form a gum. For control purposes a sample of each of the original oils was treated with ferric chloride in the same manner. The gums which were obtained were compounded with a 25-volume loading of Cellite 505 and 2% benzoyl peroxide. Some of them, particularly those formed from the 9996-1000 oil, gave fair press cures after milling. However, all of them shrank and blistered in the oven cure. The fact that the same behavior is noted when a small amount of silicone oil is

added to standard stocks would indicate that unreacted oil is present after the selenium dioxide treatment. Techniques for eliminating this unreacted oil will have to be developed.

C. Reaction of Silicone Gum with Selenium Dioxide

The milling of General Electric silicone gum 9979-G with 10 parts of selenium dioxide at the standard 25 volume loading with Celite 505 produced a stock which cured satisfactorily in a press (15 minutes at 350°F), whereas a control batch of gum and Celite yielded a crumbly, uncured mass. Further work on developing optimum conditions for curing with  $\text{SeO}_2$  is in progress. The toxic effect of  $\text{H}_2\text{Se}$  has been somewhat of an obstacle in this study, and techniques for removal of the toxic fumes during cure are being investigated.

## VII. STUDIES ON THE PREPARATION OF SILICONE GUMS

It has been decided to institute a program on the preparation of silicone gums starting with either the monomers or the silicone oils. This program has become necessary as results of other attacks yield increasing evidence that compounding techniques (i.e., physical changes) are not likely to lead to great improvement in the properties of silicone stocks. Alteration of the chemical nature of the base polymer can be accomplished either by (a) starting with different monomers; (b) modifying the polymerization conditions by adding materials other than water in the hydrolysis step (alcohols, for example); or, (c) chemical reaction of the gum in a depolymerized state is discussed in Section IV of this report. To date no attempt has been made to synthesize various monomers which might be of interest, but it is intended to initiate such studies soon. The other possibilities noted above have been subjected to preliminary investigation during this period.

One of the interesting possibilities under investigation involves adding dimethyldichlorosilane to a mixture of water and polyvinyl alcohol. Such a procedure might be expected to lead to a chemical combination of polyvinyl alcohol and silicones with the product retaining some of the properties of both. The procedure has been found to yield viscous slurries

which form very tough and flexible films on exposure to air. These films are tougher than either polyvinyl alcohol or silicone gum, but are not heat stable, showing marked embrittlement at 212°F. The products of the combined hydrolysis and alcoholysis can be treated with ferric chloride solutions to yield gums. These gums are under investigation.

Another phase of this work which is receiving attention involves formation of gums from chlorinated silicone oils. These methyl siloxane compounds are easily chlorinated in the presence of ultraviolet light to yield chloromethyl groups with the degree of chlorination being easily controlled. Such chlorinated oils have been treated with ferric chloride solution to yield gums.

Under the typical curing cycle employed for standard stocks, the gums from the chlorinated oils show poor cures. It therefore seems that the subsequent curing conditions for these products must be modified to determine the optimum time and temperature cycle.

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